Synthesis and Magnetic Properties of Crystals Bi$_2$BaFe$_4$O$_{10}

Abstract. *The paper presents the results of an experimental study of the first synthesized compound in the system Bi$_2$O$_3$-BaO-Fe$_2$O$_3$. It was found that the compound has cubic symmetry, the lattice parameters was determined. Electron microscopy measurements reveal that, in general, elemental composition of different parts of the samples corresponds to Bi$_2$BaFe$_4$O$_{10}$ formula. According to magnetic measurements, the compound has a magnetic order with the magnetic ordering temperature T$_C$ = 700 K.*

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The interest in systems, which simultaneously have several types of magnetic order (multiferroics) [1] is due to both potential practical applications and solution of a number of fundamental condensed matter physics problems. One of the first and most studied materials in this class is the crystal BiFeO$_3$ [2, 3], which has high electric (T$_C$ $\approx$ 1100 K) and magnetic (T$_N$ = 643 K) ordering temperatures. It is known that magnetic properties are determined by the presence of transition element ions (3d- or 4f-ions), and the ferroelectric properties of model oxide compounds are determined, as a rule, by the presence of "heavy" elements in a state with empty d-orbitals [4], for example, pairs of Bi^{3+} or Pb^{3+} ions. The development of new multiferroics is aimed both at searching for new crystals and at creating synthetic structures (in particular, multilayer film structures).

Interest in nanoscale multiferroics has noticeably increased [5]. In this case, wider opportunities to design materials with specified characteristics are available and new properties that are not inherent in bulk materials are manifested. Such an approach as the creation of powders or layered systems based on known materials [6], for example, ferroelectric-magnetic spinel, is being developed. Some progress

has been made in the BiFeO$_3$-CoFe$_2$O$_4$ system. However, a simple mechanical mixing of the source materials does not allow the creation of fundamentally new compounds.

Interest in magnetic, ferroelectric and piezoelectric properties of based on bismuth oxides has recently increased. Therefore, we attempted to obtain a chemically synthesized nanosized compound with the properties of Bi-based multiferroics to understand what chemical and structural factors affect magnetic ordering.

Taking into account the high aggressiveness of Bi$_2$O$_3$-based melts to various crucible materials (including Pt), the compound Bi$_2$BaFe$_4$O$_{10}$ was obtained by solid-phase synthesis from initial oxides (special purity). The crystals were synthesized from a mixture of ultra-pure oxides Bi$_2$O$_3$, Fe$_2$O$_3$ and analytically pure alkali-earth metal carbonates with appropriate stoichiometry. Solid-phase synthesis was carried out on the basis of thermal data on the initial components, taking into account the Tamman's conditions for ceramic reactions. First, a preliminary annealing of the calculated mixture of initial components was made, for which they thoroughly mixed and rubbed into an agate mortar. Then, to activate the initial materials, they were crushed on a ball planetary mill for 10-20 minutes, after which they were placed in alundum crucibles and annealed in a silicate furnace. Annealing included four stages. The first stage is 600 °C for 12 hours, then 700 °C for 12 hours, 800 °C for 12 hours, and 900 °C for 5 hours.

X-ray studies were carried out using a Miniflex 600 diffractometer (Rigaku), electron microscopic studies were performed using a microscope JSM-7001F \# 630 (JEOL), distributions of crystallites in size were obtained using the CPS Disc Centrifuge, Model DC 24000, and magnetic measurements were carried out using magnetometer MPMS-XL, working on the basis of the quantum interference effect.

The Fig.1 shows the X-ray diffraction pattern of the synthesized samples. The crystals have a cubic syngony with the lattice parameters a = b = c = 3.9216 \AA. The X-ray density of the substance is equal to ρ = 7683 kg/m^3.

Electron microscopic images of crystallites showed that there is a considerable dispersion in the size of the crystallites. An estimation of the obtained crystals' elemental composition was made, for which microprobes were taken from different parts of the powder. In general, the elemental composition in different parts of the samples corresponds to the nominal value. If the compound formula is written in the form Bi$_x$Ba$_y$Fe$_z$O$_{10}$, the content of the elements is in the range x = 1.8 -- 2.1, y = 1, z = 3.7 -- 4.1. The question of the oxygen content remains open. At the same time, a regularity is noted that the larger the crystallite, the closer it is to its nominal value.

The inset of the Fig.1 shows the distribution function f(d) of crystallites in size. A maximum of distribution in this technology for producing Bi$_2$BaFe$_4$O$_{10}$ polycrystals occurs at d $\approx$ 1.5 μm. As can be seen from the distribution curve, the particle size array is mainly confined in

the region <6 μm. The entire range of distribution of particles (blocks) in size ranges from 50 nm to 30 μm (individual crystallites).

The field dependences of the magnetization M(H) at temperatures T = 4 K and T = 300 K are shown in Fig. 2. The magnetization was measured in fields up to 4 MA/m. As seen in the figure, the curves have a typical ferromagnetic form. The hysteresis loops "collapse" in the vicinity of the field H$_S$ $\approx$ 400 kA/m, and then a paraprocess is observed. The slope of the straight part of the M(H) curve has the same value in the field range H = 0.8 -- 4 MA/m, and this is observed both in helium temperatures and in room temperatures. It is also seen that the coercive force is small and accounts for H$_C$ $\sim$ 8 kA/m.

Fig. 3 shows the temperature dependence of the magnetization taken in the field H = 400 kA/m. The M(T) curve demonstrates that magnetic ordering takes place. The inset shows the temperature dependence of dM/dT, from which it follows that the magnetic ordering temperature T$_C$ $\approx$ 700 K.

To understand the results, it is necessary to decide what material we are dealing with. Above all, it follows from the value of the coercive field, that the resulting crystal has a small magnetic anisotropy. Since only the iron ion is the magnetoactive center, it must be in the trivalent state (state ^{6}S). If the valence states of the elements are preserved, from the chemical formula of the compound Bi$_2$BaFe$_4$O$_{10}$ = Bi$_2$O$_3$ + BaO + 2$\cdot$Fe$_2$O$_3$ the following combinations can be proposed: 1) BaFe$_2$O$_4$ + 2$\cdot$BiFeO$_3$, 2) BaFe$_4$O$_7$ + Bi$_2$O$_3$, 3) Bi$_2$Fe$_4$O$_9$ + BaO, and 4) BiBaFeO$_4$ + BiFeO$_3$ + Fe$_2$O$_3$. No traces of Bi$_2$O$_3$ and BaO were found in the X-ray diffraction pattern. This means that compounds of the BaFe$_4$O$_7$ and Bi$_2$Fe$_4$O$_9$ type should not form, especially since they have a noncubic symmetry and do not appear in X-ray spectra. Cases 2) and 3) therefore are excluded from consideration. Crystals BiFeO$_3$ (T$_C$ $\approx$ 643 K), α-Fe2O3 (T$_N$ $\approx$ 960 K) and BaFe$_2$O$_4$ (TC $\approx$ 726 K) also have a noncubic symmetry and the magnetic transition temperatures that do not coincide with the temperature determined during this experiment. As a result, we find that the Bi$_2$BaFe$_4$O$_{10}$ phase should be dominant. The BiBaFeO$_4$ phase (not yet described in the literature) can also be present, but this compound must be paramagnetic because of the low iron content.

It is possible that the last mentioned phases may be present as impurities, but their content is extremely small and does not appear in the x-ray spectrum and in the magnetic behavior. For more detailed studies, additional methods such as electron magnetic resonance and Mossbauer spectroscopy will be involved.

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